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A CRITICAL STUDY OF THE BURRELL INDICATOR FOR COMBUSTIBLE GASES IN AIR

BY

LOWELL H. MILLIGAN

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A CRITICAL STUDY OF THE BURRELL INDICATOR FOR COMBUSTIBLE GASES IN AIR

By Lowell H. Milligan

INTRODUCTION

Early in the history of coal mining the hazards to life and property from ignitions and explosions of fire damp (methane and air) were recognized. The safety lamp introduced by Davy in 1815 did much to increase the safety of miners; the modified Davy lamp is still the indicator most widely used in gaseous mines for detecting the presence and approximate amount of combustible gas in the mine atmosphere.

However, the safety lamp has limitations as a gas indicator, and it is doubtful whether an average observer can detect less than 1 per cent of methane, the combustible gas present in mines, with the type ordinarily employed. Even a skilled mine inspector with a good lamp can seldom discover 0.75 per cent, and never definitely detect 0.5 per cent or less. When there is enough methane present to be detected with the lamp, the amount may be roughly estimated, but these estimates are likely to differ by 0.5 to 1 per cent or more from the true value.[1]

When there is between 5½ and 15½ per cent of methane in air an explosive mixture is formed; but this is not the only cause of mine explosions. Dry coal dust suspended in air is explosive, and coal-dust explosions are propagated more rapidly and disastrously when gas is present in proportions much below the explosive limit. The amount of gas in mines must, therefore, be kept as low as possible by proper ventilation. For safety, the proportion of methane in return airways should be kept less than 0.5 per cent. One method of checking the condition of a mine as to gas, in addition to the common system of "fire bossing" with safety lamps, is to systematically analyze samples of return air currents. Comparison of these analyses gives a general daily check on the freedom from gas of those portions of the mine ventilated. There is a demand in the mining industry for a simple instrument which will quickly determine small quantities of methane in mine air with a moderate degree

[1] Paul, J. W., Use and care of miners' safety lamps: Miners' Circular 12, Bureau of Mines, 1913, pp. 11-13. Paul, J W., Ilsley, L. C., and Gleim, E. J., Flame safety lamps: Bull. 227, Bureau of Mines, 1924, pp. 165-197. Cadman, John, and Whalley, E. B., Reports of an inquiry into the ventilation of coal mines, and the methods of examining for fire damp: Royal Commission on Mines, London, 1909, p. 63.

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of accuracy, which is not too expensive and is easily portable, strong and safe.

In an effort to meet this demand, the Burrell methane indicator in its first form [2] was developed at the Pittsburgh experiment station of the Bureau of Mines in 1915 by G. A. Burrell, in collaboration with G. A. Hulett and O. P. Hood. It was then termed the "Burrell gas indicator" or "gas detector." The writer, assisted by J. J. McKitterick and D. O. Crites, under the general direction of Mr. Burrell and of A. C. Fieldner, supervising gas chemist, made improvements in the original model. This instrument is now equipped with a large gage glass and 4 per cent methane scale; and, having met the specifications of Schedule 8A[3] of the bureau, it has been officially approved under this schedule.

Although intended primarily for use in mines, the Burrell indicator may be adapted to the analysis of mixtures of air with any other single combustible gas or vapor (such as hydrogen or gasoline vapor) which is practically insoluble in water, and of which the average composition is known. It is used on U. S. Navy submarines to test for hydrogen which is liberated by the storage batteries and may become dangerous.

This paper describes the Burrell methane indicator, its principle, and operation, gives a few typical results representing numerous actual mine tests, and discusses the possible sources of error and the effect that errors may have on the accuracy of determinations. The use of the indicator for other combustible gases is described, and differences are pointed out. Finally, the calibration of the indicator is considered both theoretically and experimentally.

ACKNOWLEDGMENTS

Besides those already mentioned as collaborating in the development work, the author is indebted to L. C. Ilsley, E. J. Gleim, and other members of the electrical section of the bureau, who made the official approval tests of the indicator. They gave many helpful suggestions and supplied the electrical data given herein. With the able assistance of G. W. Jones, W. P. Yant, and others in the gas laboratory, much has been accomplished that otherwise would have been impossible. Mr. McKitterick made tests in different coal mines, and the Bureau of Mines is indebted to many employees of the coal companies operating these mines for their cooperation. The staff of the experimental mine of the bureau assisted materially in tests of the indicator, and have suggested improvements based on their experience.

R. E. Hall, C. M. Bouton, G. W. Jones, and S. H. Katz criticized the manuscript of this paper.

[2] Burrell, G. A., Description of a portable gas detector: Jour. Ind. Eng. Chem., vol. 8, 1916, p. 365.

[3] Procedure for establishing a list of permissible methane indicators for mines: Schedule 8A, Bureau of Mines, Aug. 25, 1920, 9 pp.

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THE BURRELL METHANE INDICATOR

DESCRIPTION AND METHOD OF OPERATION

A Burrell indicator, attached to an Edison storage battery of the type used for miners' portable electric cap lamps, is shown in Plate I, *A*. Plate I, *B*, illustrates the method of using the indicator to determine the percentage of methane in mine air. Figure 1 is a detail section of the indicator.

The indicator is really a special type of gas-analysis apparatus for determining the percentage of methane in air by slow combustion; it uses a platinum-wire "glower" at bright yellow heat to burn out the gas. In the ordinary apparatus [4] for gas analysis, the volume of the sample of mine air is measured, the methane is burned out of it, and the volume of the residual gas is measured. The difference between the volume of the sample and that of the residual gas is the contraction which has taken place on burning and is twice the volume of the methane originally present. Methane burns according to the following reaction:

CH_4	+	$2O_2$	=	$1\ CO_2$	$(+2\ H_2O)$
1 volume methane		2 volumes oxygen (from air)		1 volume carbon dioxide	0 volume water

Water condenses at ordinary temperatures to a liquid, and as such occupies a negligible volume. From the volume of methane calculated from the contraction and the volume of the original sample it is easy to calculate the percentage volume of the methane originally present.

The indicator (see Fig. 2) is essentially a U-tube about three-fourths filled with water. To make a test the water in the large reservoir is forced up into the valve cup by blowing into the rubber tube, and when allowed to return to the normal position shown in Figure 2 it draws in a sample of mine air through the valve. The level of the water, therefore, defines the volume of the air sample taken. The valve is closed and the methane is burned out of this sample by the hot glower. The contraction that results is shown by the new position of the water level in the gage glass next to the scale marked to read directly in percentage of methane. The instrument is designed with definite values for the volume of the gas sample and the inside diameter of the gage glass, and these must be correct or the indication will not be accurate. While the methane is burning the heat causes the volume of the gas to increase, but water is merely forced up into the return reservoir and none is lost. Shaking the indicator before and after combustion brings the temperature of the gases to that of the water and permits them to come to a definite state of equilibrium by being either dissolved in or liberated from

[4] Jones, G. W., The Bureau of Mines Haldane apparatus; its application and instructions for use: Report No. 299-B-70; Bureau of Mines, 1922, 49 pp. Available in mimeographed form.

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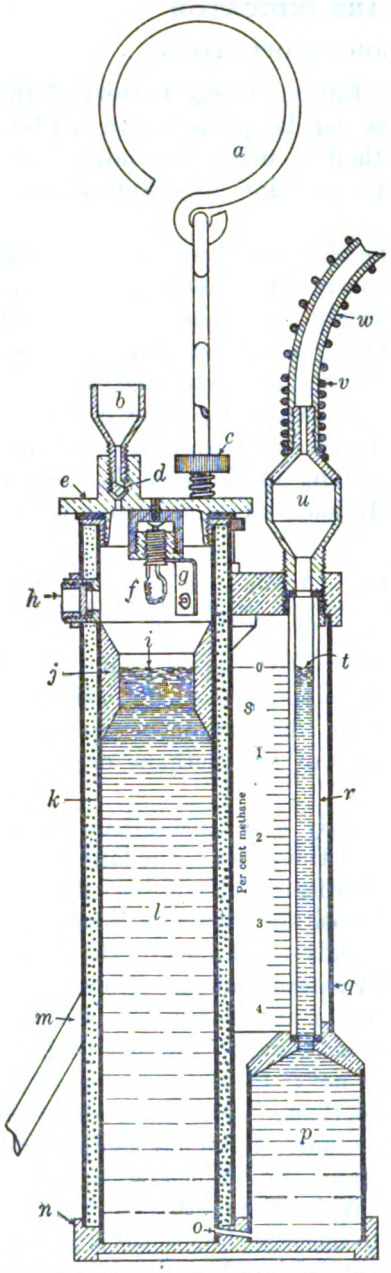

FIGURE 1.—Detail section of Burrell methane indicator: *a*, Handle; *b*, valve cup; *c*, electric switch; *d*, valve; *e*, cover; *f*, glower; *g*, electric contact spring; *h*, window; *i*, water level; *j*, collar; *k*, heat-insulating material; *l*, large reservoir; *m*, electric cord; *n*, base; *o*, communicating passage; *p*, small reservoir; *q*, gage-glass guard; *r*, gage glass; *s*, methane scale; *t*, water level; *u*, return reservoir; *v*, protecting spring; *w*, rubber tube

solution in the water. The scale of the indicator was not calculated directly from a contraction basis, but was made so as to include such factors as solubility.

DIRECTIONS FOR OPERATING THE METHANE INDICATOR

The Burrell methane indicator is operated as follows:

1. Carefully remove the cover (see Fig. 2), put distilled water in the indicator, and adjust the water level to zero of the scale.

2. Be sure that the glower is in good condition. The turns of the filament should not be distorted and should be evenly spaced. If there is a cap on the glower (used as a protection in shipment) carefully unscrew it and leave it off.

3. Replace the cover and test the indicator to make sure that it is air-tight, by closing the valve and blowing into the rubber tube. Pinch the tube when the water surface is near the bottom of the gage glass, and hold it for 15 seconds; then release it. If the water does not rise again to zero on the scale, the indicator leaks. The cover probably needs to be screwed down tighter.

4. Select a battery that has been fully charged. (With normal charging current, full charge is indicated when the potential across each of the two cells of the Edison battery reaches a value between 1.8 and 1.9 volts. The potassium hydroxide solution in the cells should have a specific gravity of about 1.200.) *Caution:* To prevent possible burning out of the glower, the battery should not be attached to the indicator until at least two hours after it has been taken off charge.

5. Test the electrical contacts of the indicator by noting whether the glower becomes bright yellow when the switch is screwed down.

6. When ready to make a test for methane, see that the water level stands at zero when the valve is opened. Then, with the valve open about an eighth of a turn, blow into the tube until water can be seen in the cup of the valve. Close the valve to keep the water in this

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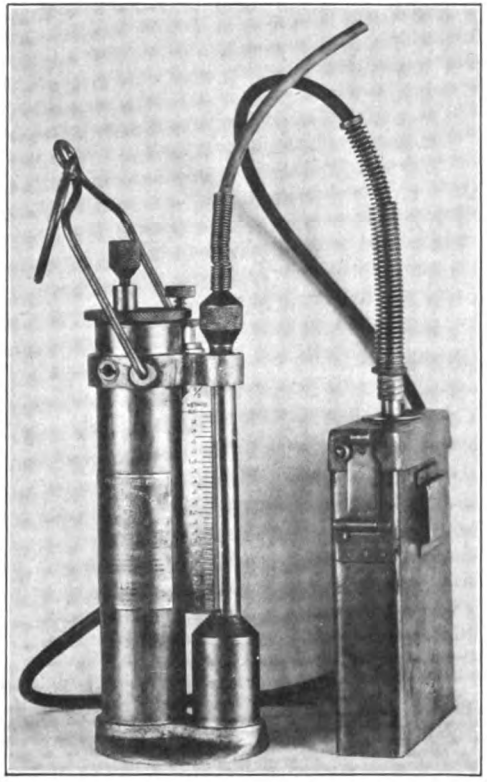

A. THE BURRELL INDICATOR COMPLETE WITH BATTERY

B. MAKING A TEST

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position. (The cup must not overflow, because loss of water will lower the zero water level.)

7. Hold the indicator in the place from which the sample is desired; open the valve and allow the gas sample to enter the indicator until the water level comes again to zero on the scale. Then close the valve. (If the operator is in a moving air current, he should face it when taking a sample.)

8. Grasp the handle of the indicator with one hand, hold the base with the other, and shake the indicator up and down vigorously for one minute. Note carefully the position of the water level for any correction to be applied to the final reading. (That is, if the water is one division below the zero level, 0.1 per cent should be subtracted from the final reading. If the water level is above zero, the correction should be added to the final reading.)

9. Close the switch. If the glower does not light up at once, shake the instrument gently from side to side to remove any water that may be caught in the glower, which must appear bright yellow during the entire combustion or the results will be too low.

10. After the glower has burned for two minutes, open the switch, grasp the handle and base as in (8), and shake the indicator up and down vigorously for one minute. If any air bubbles are present in the gage glass, remove them by first blowing into the tube until the water level just disappears, and then slowly releasing the pressure. Read at once the percentage of methane indicated on the scale opposite the final position of the water level in the glass, correcting it if necessary as noted in (8).

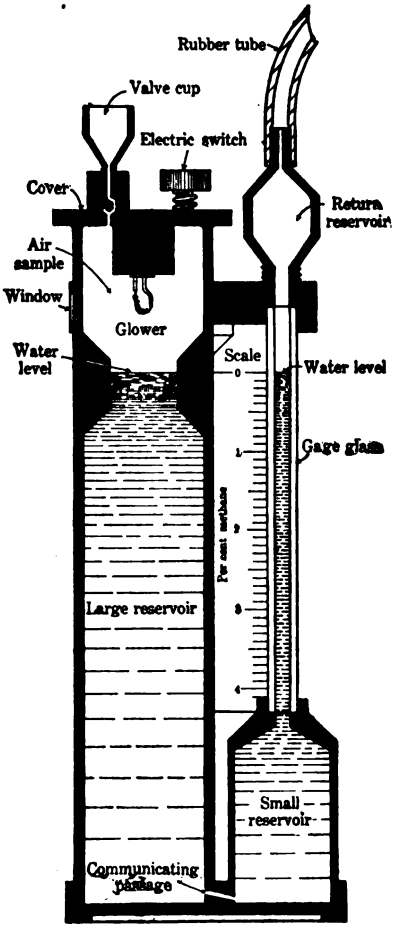

FIGURE 2.—Simplified section of indicator

An alternate procedure to obviate the necessity of correcting the final reading is an advantage if the water tends to rise much above the zero level when the indicator containing the sample is shaken. By this procedure the sample is allowed to enter the indicator only to the point where the water level appears in about the middle of the gage glass and the valve is quickly closed to hold it in this position. The indicator is shaken as in (8), then held in the position from which the sample was taken, and the valve opened. When the water level has come to zero the valve is closed and the directions in (9) and (10) are followed, except that no correction of the final reading is necessary. When maximum accuracy

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is desired, two samples of the same gas mixture should be run successively, and the second result taken as the more accurate.

The first indication obtained with the instrument each day will probably be too high (due to the solubility of air in water which has stood in the indicator for a number of hours) and should be discarded. The inside of the indicator should be rinsed out and the water replaced with fresh distilled water every few months.

The temperature of the indicator must be approximately that of the mine air. If there is reason to believe that the difference is somewhat more than 2° F., two determinations should be made and the first reading discarded. When temperature differences are wide, some time should be allowed before determinations are started. A determination should be completed at the place where the sample is taken, as this helps to avoid temperature changes. When maximum accuracy is desired in cold weather, the operator is advised to wear gloves to prevent the heat of his hands from being transmitted to the instrument.

The method of shaking the indicator is important. Shaking up and down through a distance of about 12 inches twice a second has proved most satisfactory. The water in the large reservoir must be thoroughly shaken up into the space that contains the gases, but a shaking violent enough to throw some water out of the gage glass should be avoided.

In order to test the ability of the operator, determinations may be made on room air that contains no combustible gas.

The glower must be at bright yellow heat for two minutes. All of the methane will not burn in a shorter time. If the glower is kept hot too long, the indicator is overheated and the battery run down unnecessarily. Under especially favorable conditions, 40 determinations have been made with one fully-charged battery without recharging. The battery must supply enough current to keep the glower at bright yellow heat during the entire combustion or results will be too low. Care must be taken to see that the battery has stood "off charge" for several hours before it is used, because an Edison cell that has just been removed from the charging apparatus has an abnormally high voltage and will be likely to send enough current through the glower to burn it out, especially when the samples being analyzed contain much combustible gas, as this raises the glower temperature. The new switch design shown in Figure 3 (p. 10) and better specifications for the glowers, insuring the proper "hot resistance," will avoid the likelihood of this happening.

The battery should not be left attached to the indicator overnight, as the current frequently leaks slightly across the moist contacts within the indicator; this leakage will in time exhaust the battery unnecessarily.

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The inside diameter of the gage glass must be correct, and therefore only the glasses supplied by the indicator manufacturer should be used.

To prevent the indicator being taken apart in places containing combustible gas, the top may be sealed on by running a wire through two of the holes provided for the purpose, and fastening it with a lead seal. Tests by the Bureau of Mines in connection with official approval showed that the indicator is strong and safe. The battery and the indicator must be properly connected, however, with the same wire grounded on the indicator that is grounded on the battery case; otherwise the battery would become discharged if the indicator and battery casing were kept in contact with each other. A sample of an explosive gas mixture explodes when the glower is turned on, but the flame does not escape from the instrument.

The indicator is intended for analyzing air containing not more than 4 per cent of methane, which corresponds to the full-scale indication. Mixtures containing gas up to the upper explosive limit (15.5 per cent) are readily recognizable because they explode inside the instrument. More than this proportion of gas gives low indications which are misleading and have no value, but such mixtures will not be found if the air analyzed is supporting human respiration. The first reading after an explosive mixture has been sampled should be discarded.

The tests for accuracy[4a] which the indicator had to meet for approval are as follows:

Tests for accuracy

Methane present, per cent	Minimum indication of methane, per cent	Maximum indication of methane, per cent	Permissible error in the indication of methane, per cent
0.25	0.10	0.40	±0.15
0.50	0.35	0.65	±0.15
1.00	0.80	1.20	±0.20
2.00	1.80	2.20	±0.20
3.00	2.70	3.30	±0.30
4.00	3.70	4.30	±0.30

Under favorable conditions an experienced operator can more than double this accuracy. Obviously all the results are expressed in terms of percentage by volume of the original air sample.

[4a] This paper frequently mentions the amount that any indication is in error. Errors and variations are expressed as the difference between the true percentage of the gas present and the percentage found by analysis with the indicator, as shown in the above table. Thus if 0.94 per cent methane was actually present and the indicator showed 0.98 per cent, the error or the variation between the reading and the true value would be said to be +0.04 per cent methane.

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MINE TESTS WITH THE METHANE INDICATOR

The methane indicator has been thoroughly tested in mines by comparing the results of determinations made with it and accurate analyses of samples of the mine air taken at the same time in vacuum bottles and later analyzed with the Haldane apparatus [5] in the laboratory. As would be expected, agreement between the results for samples taken close to the source of the methane in a mine was not as good as the agreement at points where there had been ample opportunity for the methane and the air to mix thoroughly. Sudden variations could often be traced directly to temporary changes in ventilation through the removal of brattices or the opening of mine doors.

Tables 1 and 2 give all the results of tests in two different mines and are representative of a large number of tests made by an experienced operator. Table 3 gives the results obtained with the indicator when used to control the amount of Pittsburgh natural gas added to the air in the experimental mine of the bureau at Bruceton, Pa., where tests of the explosibility of coal dust are made. Each table gives all indications obtained during consecutive tests in which gas was used, selected at random from the reports for two years. At the experimental mine the indicator was used by different operators. A determination was not started and completed at the same place, as the instructions specify, but the sample of mine air was taken at one place and the indicator carried to the next station while the sample was being burned. These tests show the general accuracy obtainable when the Burrell methane indicator is used in actual practice.

TABLE 1.—*Results with methane indicator fitted with large gage glass, at Consolidation Coal Co. mine 43, monongah, Marion County, W. Va., July 11, 1918. Mine entered at 7.45 a. m.*

Test No.	Place in mine	Time	Methane indicated	Haldane analysis		Error in methane indicated
				Methane	CO_2	
			Per cent	*Per cent*	*Per cent*	*Per cent*
1	No. 2 north return	8.15 a. m.	0.40			
2	"	8.35 a. m.	0.20	0.25	0.10	−0.05
3	"	8.52 a. m.	0.32			
4	"	9.00 a. m.	0.28			
5	"	9.18 a. m.	0.28			
6	"	9.30 a. m.	0.30	0.32	0.10	−0.02
7	Face No. 7, right butt	10.05 a. m.	0.29			
8	"	10.15 a. m.	0.32	0.42	0.05	−0.10
9	"	10.25 a. m.	0.32			
10	"	10.37 a. m.	0.33	0.43	0.05	−0.10
11	No. 7 right return	11.05 a. m.	0.35			
12	"	11.15 a. m.	0.28	0.31	0.10	−0.03
13	No. 7 right intake	11.28 a. m.	0.22	0.21	0.08	+0.01
14	Additional air course	12.00 m.	0.00			
15	"	12.10 p. m.	0.08	0.00	0.05	−0.08
16	Main slope return	12.30 p. m.	0.11	0.14	0.14	−0.03
17	"	12.40 p. m.	0.10			

Average error (disregarding signs) = 0.05 per cent methane.
Maximum error = 0.10 per cent methane.

[5] Jones, G. W., work cited.

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TABLE 2.—*Results with indicator fitted with large gage glass, at Consolidation Coal Co. mine 86, Carolina, Marion County, W. Va., July 12, 1918. Mine entered at 10 a. m.*

Test No.	Place in mine	Time	Methane indicated	Haldane analysis		Error in methane indicated
				Methane	CO_2	
			Per cent	*Per cent*	*Per cent*	*Per cent*
1	Return; No. 1 south face	10.05 a. m.	0.50	0.56	0.07	−0.06
2		10.25 a. m.	0.40			
3		10.38 a. m.	0.46			
4		10.43 a. m.	0.52			
5		10.53 a. m.	0.46			
6		11.05 a. m.	0.47	0.52	0.06	−0.05
7	Right entry; No. 1 south	11.35 a. m.	0.59	0.61	0.08	−0.02
8		11.43 a. m.	0.59			
9		11.53 a. m.	0.56			
10		12.00 m.	0.60			
11		12.08 p. m.	0.53			
12		1.05 p. m.	0.60			
13		1.15 p. m.	0.54	0.61	0.07	−0.07
14		1.20 p. m.	0.54			
15	Near face left entry	1.35 p. m.	0.54			
16		1.42 p. m.	0.55	0.60	0.06	−0.05
17		1.52 p. m.	0.60			
18		2.02 p. m.	0.63			
19		[a] 2.12 p. m.	[a] 0.90	[a] 0.78	0.15	[a] +0.12
20		2.25 p. m.	0.53			
21	No. 1 south face; right entry	2.42 p. m.	0.65			
22		2.51 p. m.	0.61	0.65	0.07	−0.04
23		2.59 p. m.	0.61			
24		3.05 p. m.	0.56			
25		3.17 p. m.	0.57	0.50	0.07	+0.07
26		3.24 p. m.	0.57			

[a] Ventilation was temporarily affected at this point because a cloth brattice had been taken down and a door inserted in its place. The maximum error occurred here.

Average error (disregarding signs) =0.06 per cent methane.
Maximum error =0.12 per cent methane.

TABLE 3.—*Results with indicator fitted with large gage glass, for analysis of air containing natural gas, at the Bureau of Mines experimental mine. (Data copied from explosion test sheets)*

Test No.	Date	Place in mine	Height of cap on flame of safety lamp	Methane indicated	Haldane analysis, total hydrocarbons [a]	Difference [a]
			Inch	*Per cent*	*Per cent*	*Per cent*
510	Apr. 23, 1919	E-1300	0.3	1.16	1.04	+0.12
	do	A-950	.3	1.10	1.00	+0.10
	do	A-550	.3	1.08	1.06	+0.02
	do	A-250	.3	1.00	1.03	−0.03
511	Apr. 24, 1919	E-1300	.3	0.91	0.93	−0.02
	do	A-550	.3	0.88	0.84	+0.04
	do	A-250	.3	0.88	0.87	+0.01
512	do	E-1300	.3	0.80	0.85	−0.05
	do	A-950	.3	0.79	0.61	+0.18
	do	A-550	.3	0.90	0.85	+0.05
513	do	E-1300	.4	1.62	1.61	+0.01
	do	A-950	.4	1.63	1.59	+0.04
	do	A-550	.4	1.80	1.68	+0.12
	do	A-250	.4	1.93	1.82	+0.11
572	Mar. 15, 1920	E-1300	.3	1.3	1.3	0.00
	do	A-950	.3	1.15	1.19	−0.04
	do	A-550	.3	1.15	1.22	−0.07
	do	A-250	.3	1.1	1.15	−0.05
574	Mar. 30, 1920	E-1300	.3	1.25	1.30	−0.05
	do	A-750	.3	1.20	1.30	−0.10
	do	A-250	.3	1.15	1.20	−0.05
575	Mar. 31, 1920	E-1300	.4	2.10	2.11	−0.01
	do	A-250	.4	2.15	2.28	−0.13
577	Apr. 5, 1920	E-1300		2.05	1.87	+0.18
	do	A-250		2.10	2.07	+0.03
578	Apr. 7, 1920	E-1300	.3	0.95	1.06	−0.11
	do	A-250	.3	1.00	1.10	−0.10
579	Apr. 9, 1920	E-1300	.3	1.05	1.01	+0.04
	do	A-250	.3	1.00	1.04	−0.04

[a] The "total hydrocarbons" in Pittsburgh natural gas consist approximately of 90 per cent methane and 10 per cent ethane. A Burrell indicator accurately calibrated for methane should read slightly high for this natural gas; or if calibrated for total hydrocarbons in Pittsburgh natural gas should read slightly low when used for pure methane (see p. 11).

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MODIFICATION OF SWITCH DESIGN OF INDICATOR TO INCREASE LIFE OF GLOWER

The peak voltage of freshly charged batteries is abnormally high, and when such batteries are connected to the indicator just after being removed from the charging apparatus there is danger of burning out the glower, especially when an air sample containing considerable combustible gas is being analyzed. On this account it is specified in the instructions for using the indicator that the battery should stand off charge for at least two hours before use. Often this procedure is inconvenient, and it is proposed that the design of the switch be modified to overcome this difficulty.

This modified switch design is shown diagrammatically in Figure 3. An auxiliary brass contact-spring and an auxiliary resistance wire, marked *c* and *e*, have been inserted between the contact screw *a* and brass contact *d* with which the indicator is at present equipped. The contact screw *a* is grounded on the metal frame of the instrument, as is the brass screw *i*, while the remaining parts of the electric circuit shown in black in Figure 3 are carefully insulated from the frame. When, therefore, the contact screw *a* is unscrewed and does not touch *c*, the glower circuit is open and the glower *g* does not burn. As *a* is screwed down, the spiral spring *b* prevents loose action. When *a* touches *c*, electric contact is made through the auxiliary resistance *e*, which consists of a 3-inch length of double cotton-covered B. & S. gage No. 29 manganin wire, resistance 2.45 ohms per foot, and the glower burns with only a red heat even when attached to a freshly charged battery. A 10-second burn in this position suffices to remove most of the peak voltage from the battery. Then *a* is screwed completely down, so that contact is made between *c* and *d* directly, as is shown by the dotted outline in Figure 3. This short-circuits the auxiliary resistance and permits the glower to come up to its bright yellow heat. The remainder of the combustion period is completed with this setting of the switch.

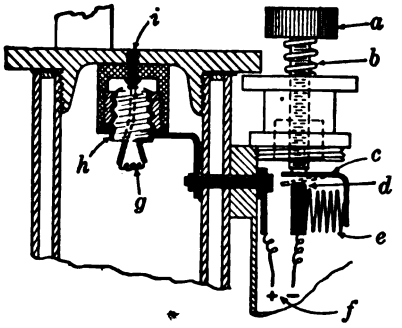

FIGURE 3.—Modification of the switch design of the indicator in order to increase the life of the glower: *a*, Electric contact screw; *b*, spiral spring; *c*, auxiliary brass contact spring; *d*, brass contact; *e*, auxiliary resistance wire; *f*, electric cord to battery; *g*, glower; *h*, glower socket; *i*, brass screw grounded to frame

An experimental indicator was fitted with this device and functioned satisfactorily, although of course extended usage may bring out unforeseen minor difficulties. It may be more satisfactory to make the auxiliary brass contact-spring *c* with the end curled under

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slightly in such a way as to scrape against the brass piece *d*, making the final contact "self-brightening."

Some new glowers on the market have had such a low electrical resistance when hot that they tended to burn out at ordinary battery voltage. Such glowers are defective, and even the use of the auxiliary resistance can not be expected to make them satisfactory.

POSSIBLE SOURCES OF ERROR IN TESTING

The factors that might influence the accuracy of the indicator are discussed in detail under the following heads: 1, Dimensions and details of the indicator; 2, temperature changes; 3, solubility of gases in the water of the indicator; and 4, battery voltage. It may seem that consideration of some of these could be eliminated by slight changes in the design or operation of the indicator, but this has not proved possible.

Some of the tests were made in the laboratory by using the indicator to analyze gaseous mixtures that were confined over water in a large aspirator bottle so arranged that samples could be easily withdrawn. Other mixtures were made up in a small testing gallery (an iron box 18 by 18 by 24 inches) and sampled from that. Some tests were made in a room containing the gas mixture, within which the operator worked as he would in a mine. Accurate analyses of the gas mixtures were made on a Haldane-type gas-analysis apparatus.[6] Pittsburgh natural gas, which, as previously stated, contains about 90 per cent of methane, was used in place of pure methane in most of the tests; and for comparison with the readings which the indicator would give with pure methane, the analyses with the Haldane apparatus were calculated to "equivalent methane" by dividing the contraction obtained on combustion by 2. In this way the results of analysis of natural-gas mixtures used as a substitute for methane were interpreted more correctly than by the procedure of simply applying the term "per cent methane" to the percentage of total hydrocarbons present (90 per cent CH_4 + 10 per cent C_2H_6) as has sometimes been done in the past (see p. 34). Mine "gas" is practically pure methane.

DIMENSIONS AND DETAILS OF THE INDICATOR

The indicator is designed to take a 31-c. c. gas sample, a value more or less arbitrarily chosen. Variations from this volume, which may be caused by having the water at the wrong level in the instrument or by inaccuracies in the manufacture of individual indicators, will cause errors in the indications; and these errors will, in general, be proportional to the amount of methane which is present in the gas sample. Assume that, due to this cause, a maximum error of

[6] Jones, G. W., work cited.

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±0.10 per cent of methane is permissible with a 4 per cent sample. This will correspond to an error of ±0.05 per cent of methane with a 2 per cent methane sample, and so on. The corresponding error in the sample volume of the indicator is approximately:

$$\frac{\pm 0.10}{4.00} \times 31 = \pm 0.8 \text{ c. c.}$$

The volume of the gas sample taken should therefore be 31.0 c. c. ±0.8 c. c. The inside diameter of the collar in the indicator is 2.2 cm., and therefore an accidental displacement of 1 mm. in the water level will change the sample volume ±0.4 c. c., which is within the allowable tolerance.

The gage glass is standardized at 5.6 mm., ±0.1 mm. inside diameter. Experimentally it was found that with a gage glass of 5.6 mm. internal diameter, analysis of an air sample containing 4 per cent of methane gives an indication equal to approximately 10.0 cm. on the scale between zero and the reading. This would correspond to a contraction of the sample equal to the volume within the 10.0 cm. of gage glass—that is, 2.46 c. c.[7] For a gage glass of 5.7 mm. internal diameter, which is just allowable, the corresponding volume is 2.55 c. c., and the difference of 0.09 c. c. introduces an error of $\frac{0.09}{2.46} \times 4.00$ per cent = 0.15 per cent methane. Like the error due to an incorrect sample volume, this error decreases when samples containing less methane are analyzed.

For some of the tests the indicator was fitted with a smaller gage glass of 3.96 mm. inside diameter, with a corresponding scale marked for a maximum indication of about 2 per cent, and subdivisions representing 0.05 per cent methane. However, the general accuracy which can be obtained with the methane indicator does not warrant the accuracy implied by the divisions of this scale; therefore official approval does not at present include this equipment, although it may sometimes be advantageous. The procedure for a determination with the indicator when fitted with the smaller glass is the same as for the permissible instrument, except that the indicator is only filled with water to the point marked "W. L." (water level) on the scale, corresponding to the 0.1 per cent of methane division, and the water level is allowed to come to this point instead of to zero at the start of a determination. When no methane is present, the heat from the glower causes the water level in the gage glass to rise from this point to the 0.0 per cent methane mark on the scale, which is an appreciable distance from the original water level.

[7] Experimental determination of the volume of water delivered by gage glasses of different diameters showed that the diameter of the gage glass calculated from the water delivered is only 0.01 mm. less than that obtained by direct measurement. In other words, the quantity of water normally adhering to the walls of the glass tube is negligible for this work.

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The glower filament is a 1-inch length of No. 38 B. & S. gage platinum wire (0.0040 inch in diameter), coiled by winding on a 0.04-inch mandril. The ends of the wire are soldered to terminals on a small screw plug, which makes the electrical contact. The coils of the filament should be evenly spaced about three sixty-fourths inch apart and curved out a little between the terminals. Under these conditions a fully charged battery will supply enough current for many determinations. Resistance tests of 50 satisfactory glowers gave an average cold resistance of 0.56 ohm (the maximum and minimum values being 0.60 and 0.52 ohm) and an average hot resistance with 2.5 volts applied of 1.63 ohms (the maximum and minimum values being 1.80 and 1.54 ohms), the ratio of hot to cold resistance being therefore about 3 to 1. When made up as described, the glowers from one lot of platinum wire were uniform enough to give satisfactory results. A different lot of platinum wire was used recently and glowers were found to have too low a resistance, which caused them to burn out easily. Probably a new specification based on the amount of current required to bring the glower to a specified high temperature would be more satisfactory than simply cutting a definite length of wire.

The filament is fragile, and when the indicator is taken apart the glower must be handled gently to keep it in the necessary good condition. If it is bent it may be straightened by careful application of a needle. Glowers are shipped with a protecting cap on them, which should be removed.

Distilled water should be used in the indicator, because its low conductivity prevents appreciable short circuiting of the electrical parts. This water should be replaced every few months to prevent the accumulation of products of corrosion and dirt. Sometimes erratic results are due to dirt which has partly clogged the communicating passage between the large and small reservoirs.

TEMPERATURE CHANGES

Determinations will be in error if the temperature of the residual gases in the indicator after the final shaking is appreciably different from the temperature of the sample when the inlet valve was closed. Since shaking for one minute both before and after the burning of the methane brings the samples and the residual gases to the temperature of the water in the indicator, the change in the temperature of the water is obviously the controlling factor. Calculation shows that a change of 1° C. at a working temperature of 10° C. will make the reading for methane in error by approximately 0.17 per cent methane.[8] Therefore even small changes in the temperature of the water will introduce relatively large errors in the analyses.

[8] $\frac{\text{Volume before}}{\text{Volume after}} = \frac{\text{Absolute temperature before}}{\text{Absolute temperature after}} = \frac{284}{283} = 100.35$ per cent. Approximately half of the change in the volume of the sample is indicated as per cent methane on the scale.

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If the temperature of the water in the indicator is different from that of the air, it will tend to approach the air temperature at a rate that will depend on the difference between the two temperatures, the velocity of the air current, whether or not the indicator is being shaken, and so on. Therefore, from heating and cooling curves determined for the indicator by putting cold or hot water in it and determining the rate at which its temperature changes under different conditions, it is possible to calculate how the indications will be affected by temperature differences.

Heating and cooling curves were made in this way for two different methane indicators. The form of these curves may be expressed by the exponential equation:

$$T_I - T_R = (T'_I - T'_R)\ e^{-kt}$$

where T_I and T_R represent the temperatures of the indicator and the room respectively after a time, t; T'_I and T'_R are these temperatures at the start of the experiment—that is, when $t=0$; e is the base of natural logarithms, namely, 2.718; and k is a constant under a definite set of conditions. Taking logarithms to the base e of this equation gives $\log_e (T_I - T_R) = -kt + \text{constant}$, and if $\log_e (T_I - T_R)$ is plotted against the time t, a straight line of slope $-k$ is obtained. Such straight lines were plotted from the experimental data, and the value of k was obtained from them. These values, which appear below, were obtained by putting cold or hot water in the indicator and measuring the rate of change of temperature under the conditions noted. Temperature was measured in degrees centigrade, and time in minutes.

Values of k for two indicators

Indicator number	192	340
	Value of k	
Hanging motionless in still air (cooling)	0.014	0.016
Hanging motionless in still air (heating)	0.014	------
Hanging motionless in air moving at 200 feet a minute (cooling)	0.040	0.035
Hanging motionless in air moving at 400 feet a minute (cooling)	0.057	0.049
Shaking about once a second in still air (cooling)	0.038	------
Shaking about once a second in still air (heating)	0.052	------

The physical significance of the constant k is seen by differentiating the original equation, which gives:

$$\frac{d\ (T_I - T_R)}{dt} = -k\left\{(T'_I - T'_R)\ e^{-kt}\right\}$$

The bracketed quantity is the difference in temperature between the indicator and the room air at any instant; therefore the time rate of change of the difference in temperature between the indicator and the air is a constant fraction of the instantaneous difference in tem-

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perature. If it be assumed, for simple calculation, that in a short time the change of temperature is so small as only to alter the difference in temperature by a negligible fraction of its total value, then under these conditions the amount which the temperature changes per minute may be calculated by multiplying k by the difference in temperature between the indicator and the air. Thus if $k = 0.014$, and the difference between the temperature of the indicator and the air is 15° C., the instantaneous rate of cooling or heating at this temperature is $15 \times 0.014 = 0.21$° C. a minute. For the same value of k and a temperature difference of 5° C., the rate is similarly found to be 0.07° C., a minute. At definite temperatures the rate of temperature change under different conditions will vary directly as the different values of k.

Experimental values in the foregoing tabulation show that when the indicator is suspended in air the value of k is independent of whether the indicator is heating or cooling within the small temperature range that is important in this work. When, however, the indicator is being shaken, its base is held in one hand, and the warmth of the hand tends to make it heat more rapidly than it cools. This results in different values of k between these latter heating and cooling curves.

On the basis of the data given, the difference in temperature between the indicator and the air which will introduce a variation of ± 0.1 per cent of methane in the indications can be approximated easily. This variation will be constant throughout the range of the indicator and will be superimposed on errors from other causes. Compensation for the change in temperature, while the indicator containing the gas sample is first being shaken, is made either by correcting the final reading or by bringing the water level to zero just before the gas is burned (the additional amount of sample taken is so small as to have a negligible effect), and therefore it is only necessary to consider the temperature change taking place during the burning and the final shaking. For simplicity in calculating the actual slight temperature change, the assumption will be made that the difference in temperature between the indicator and the room remains constant during the three minutes covered by the calculation.

The cross section of the gage glass is 0.246 sq. cm. and therefore 0.10 per cent methane, which is 2.5 mm. on the scale, corresponds to 0.062 c.c. within the gage glass. The difference in temperature to cause this change in a 31-c.c. gas sample at a mean temperature of, say, 20° C. is

$$\frac{293\ (0.062)}{31.00} = 0.58° \text{ C.}$$

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Let k_1 be the value of the constant during the burning, and k_2 the value during the shaking.

Then $2\ k_1\ (T_I - T_R)$ is the approximate change in temperature during the burning, and $k_2\ (T_I - T_R)$ is the approximate change in emperature during the shaking.

$$2\ k_1\ (T_I - T_R) + k_2\ (T_I - T_R) = 0.58°\ \text{C.}$$

$$T_I - T_R = \frac{0.58}{2\ k_1 + k_2}$$

Solving by substituting suitable values for k_1 and k_2 previously given, this equation gives the following results:

Approximate differences in temperature between the indicator and the air, which will theoretically cause an error of ±0.10 per cent methane in the indication

Air velocity	Difference in temperature °C.[a]	
Still air	+8.5	−7.1
200 feet a minute	+5.1	−4.5
400 feet a minute	+4.0	−3.8

[a] + shows that the indicator is at a higher temperature than the air; − shows that the indicator is at a lower temperature than the air.

Experimentally it is hard to check these values because of the difficulty of obtaining and measuring definite temperature differences satisfactorily, and because of the effect of other factors that change with the temperature—such as the solubility of the carbon dioxide formed by the combustion. These effects are discussed later. Experimental evidence indicates that the figures just given are of the proper order of magnitude, but are perhaps somewhat high when other variables are also considered. In general, smaller differences of temperature are allowable when the temperature of the indicator is below that of the air than when the reverse is true. In cold weather it is often advantageous partly to neutralize this difference by wearing gloves in order to prevent the heat of the hands from increasing the temperature of the indicator measurably during a determination.

In conclusion, the indicator is sensitive to changes of temperature, and for accurate work its temperature should be practically that of the surrounding air. The glower adds a definite amount of heat to the water, and this is enough to raise the temperature of the system about 0.58° C. during each determination involving a two-minute burn. The expansion corresponds to about 0.1 per cent methane on the scale, but was neglected in the construction of the scale with which the permissible indicator is now equipped. The slight rise of water in the gage glass when a sample of pure air is analyzed is due to this. It was originally thought that perhaps when a number of determinations were made in rapid succession the glower would

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heat the water enough to give erroneous results, but tests show that the indicator is not insulated sufficiently to cause this trouble.

SOLUBILITY OF GASES IN THE WATER OF THE INDICATOR

The indicator is shaken when it contains the gas sample and when it contains the residual gas, and most of the water in it is always brought to equilibrium with the various gases that may be present. The solubilities of the different combustible gases for which the indicator is used at present, and for carbon dioxide, oxygen, and nitrogen (from air), are given in Table 4. The temperatures 10° and 25° C. are considered to represent two different conditions of operation which the indicator should meet in mines and laboratories.

TABLE 4.—*Solubility of various gases in water* [a]

	Temperature, 10° C.		Temperature, 11° C.		Temperature, 25° C.	
	α	S	α	S	α	S
Methane	0.04177				0.03006	
Hydrogen	0.01955				0.01754	
Gasoline vapor (Hexane)					0.012	0.013
Gasoline vapor (Heptane)					0.017	0.019
Carbon dioxide	1.194	1.238	1.154	1.201	0.759	0.829
Oxygen	0.03802	0.0394			0.02831	0.0309
Nitrogen	0.01956	0.0203			0.01504	0.0164
Air	0.02264				0.01724	

[a] The data for gasoline vapor were obtained especially for this work. (See Milligan, L. H., Solubility of gasoline (hexane and heptane) in water at 25° C., Jour. Phys. Chem., vol. 28, 1924, pp. 494-497). The values for α for the other gases were taken from Van Nostrand's (Olsen) Chemical Annual, 1922, pp. 140-143, which gives the results of determinations made by Winkler and by Bohr and Bock. The values for S were calculated from those for α.

α is the volume of the gas when reduced to N. T. P. which will be dissolved by 1 c. c. of water at the indicated temperature and at 760 mm. pressure of the gas. S is the volume of this same amount of gas at the temperature of the experiment and at 760 mm. pressure.

For gasoline vapor the condition represented by these definitions of α and S can not exactly exist because the vapor pressure of the liquid is much less than 760 mm. at the indicated temperatures; but the coefficients can, nevertheless, be directly compared to similar coefficients for the other gases, and can be used in calculations involving the lower vapor pressures which are experimentally obtainable.

Methane is only slightly soluble in water; but the volume of the water in the indicator is large compared with the volume of the gas sample, and calculations show that appreciable amounts of methane are dissolved. The solubility of methane in water at constant temperature follows Henry's law, that the solubility of a gas is proportional to its partial pressure in the gas mixture. Since this is the case, the amount of methane which is dissolved by the water will be proportional to the amount which is present in the air and experimental calibration of the indicator will approximately correct for this factor because the gas sample is brought to equilibrium with the water by shaking for one minute each time before combustion.

The maximum amount of methane which can be read on the indicator—4 per cent—corresponds to a 31-c. c. sample containing 1.24 c. c. of methane. The amount of methane which will be dissolved

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from a sample of air containing 4 per cent of methane when shaken in the indicator is calculated as follows:

Let C_g be the concentration of methane in the gas phase at equilibrium, expressed as c. c. of methane per c. c. of gas at a total pressure of 760 mm.
C_w be the concentration of methane in the water phase at equilibrium, expressed as c. c. of methane per c. c. of water.
V_g be the volume of the methane in the gas phase.
V_w be the volume of the methane in the water phase.
V_t be the total volume of the methane.

Then:
$$V_g + V_w = V_t. \tag{1}$$

and
$$\frac{C_w}{C_g} = S$$

The volume of water in the large reservoir is 140 c. c., but when the indicator is shaken for one minute, a certain amount of diffusion takes place between the large and the small reservoirs, and this increases the effective volume of water exposed to the gas sample. The amount of this diffusion was quantitatively determined by putting pure water in the small reservoir and a colored aqueous solution in the large reservoir. The indicator was shaken for one minute as usual and then the intensity of the color of the solutions in the two reservoirs was compared in a colorimeter; it was found that the solution in the small reservoir was just 50 per cent as concentrated as that in the large one. Since the small reservoir and gage glass contain a total of 50 c. c. of water, the effective volume of the water exposed to the gases is 140 c. c. +25 c. c., or 165 c. c.
Therefore:

$$\frac{\frac{V_w}{165}}{\frac{V_g}{31.0 - V_w}} = S \tag{2}$$

Solving equations (1) and (2) for a 4 per cent methane sample:

	At 10° C.	At 25° C.
V_w = Vol. methane dissolved in water	0. 233 c. c.	0. 185 c. c.
V_g = Vol. methane in gas phase	1. 007 c. c.	1. 055 c. c.

The effect of the solubility of methane at different temperatures on the calibration of the indicator can only be quantitatively discussed in connection with other factors, and such a discussion is given in the section on the calibration of the indicator.

Shaking the indicator after combustion again brings about gaseous equilibrium, and most of the methane which was dissolved in the water will pass into the residual gases and be removed. However, if a sample high in methane is analyzed, and then immediately a sample low in methane, the second analysis will be slightly high due to the small amount of methane which remained in the water even after the final shaking of the first test, and which passed into the low sample when the indicator was shaken with it before combustion. Quantitatively, this is found to correspond to an indication of 0.13 per cent of methane on the scale when a determination on a 4 per cent

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methane sample is followed directly by one on pure air. The calculation is as follows:

At 10° C., 0.233 c. c. of methane dissolves in the water of the indicator at the beginning of the determination. After the final reading 0.047 c. c. remains dissolved in the water, as will be shown in the calculation of the theoretical calibration. When another sample is taken, the 50 c. c. of water contained in the small reservoir is mixed with that in the large reservoir, and the dissolved methane is distributed throughout the total volume. If the gas sample is pure air, it will remove $\frac{165}{190}\times\frac{1.007}{1.240}\times 0.047 = 0.033$ c. c. of the dissolved methane. Since 1.007 c. c. of methane represents a 4 per cent methane sample when burned in the indicator, 0.033 c. c. will give an indication of 0.13 per cent methane.

Similarly, the first reading obtained for a sample high in methane, with an indicator that has just been used for pure air or for low samples, will be slightly lower than later readings, because there is no methane in the water, and slightly more will therefore be dissolved from the sample.

These small variations are less when the indicator is used at higher temperatures, and only occur under the special conditions which have been described. They may be practically eliminated by making two or more consecutive determinations on the same gas mixture and discarding the first reading.

When the carbon dioxide produced by combustion of methane dissolves in water, equilibrium results according to the following reactions:

CO_2 gas $\rightleftharpoons$ Dissolved CO_2.
Dissolved $CO_2 \rightleftharpoons$ Undissociated H_2CO_3.
Undissociated $H_2CO_3 \rightleftharpoons H^+ + (HCO_3)^- \rightleftharpoons 2H^{++} + CO_3^{--}$.

However, these reactions rapidly come to a true reversible equilibrium, and at the comparatively low partial pressures in the indicator the solubility follows Henry's law. At constant temperature this is expressed by a straight-line graph like Figure 4, which may be applied to the action of the methane indicator.

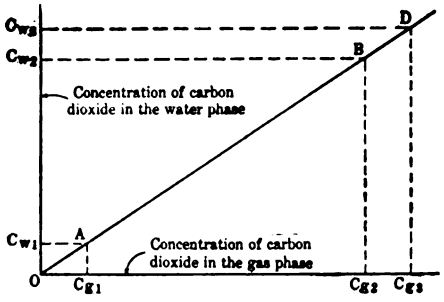

FIGURE 4.—Henry's law applied to the indicator for methane

Suppose that fresh water is put into the indicator, and that a sample of methane-air mixture containing no carbon dioxide is analyzed. If the curve in Figure 4 represents Henry's law for the temperature at which the work is being done, then after the shaking following the combustion, equilibrium will be represented by the point A, with the corresponding concentrations C_{g1}, and C_{w1}. Suppose now that a number of samples high in methane are analyzed,

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and the concentration of the carbon dioxide in the water rises: then suppose that the first methane-air mixture be again analyzed and that after shaking the indicator with the sample, equilibrium is represented by the point B. This sample is burned and the indicator is shaken. The carbon dioxide thus added equals that which was added originally and distributes itself in exactly the same way between the gas and the water phases, causing an increase in the concentration of the carbon dioxide in the gas phase from C_{g_2} to C_{g_3} and in the water phase from C_{w_2} to C_{w_3}. It is thus evident that calibration of the indicator at a given temperature is independent of the amount of carbon dioxide dissolved in the water.

When, however, the indicator is calibrated at one temperature and used at another, the different solubilities of carbon dioxide at the two temperatures have an effect which is included in the calculations (p. 28) for the theoretical calibration of the indicator.

When the effect of temperature changes was discussed, calculations were made for an allowable temperature change of 0.58° C. during a determination between the beginning of the combustion and the final reading, and the question now arises as to whether such a temperature change will ever cause the water in the indicator to liberate or absorb enough carbon dioxide in excess of that which is corrected for in the calibration to affect the results of analysis appreciably. This will be important only when gas samples containing large amounts of CO_2 are analyzed. A calculation was made of the volume change due to such absorption of carbon dioxide between 10.58° and 10.00° C. for a sample containing approximately 14 per cent of CO_2, which is probably a much higher figure than ever will actually be obtained. The result was converted to terms of the scale which indicates percentage of methane, and it was found that the corresponding error appears as 0.02 per cent methane on the scale. For smaller temperature change during a determination, or at a higher temperature or lower partial pressure of carbon dioxide, this error will be less. The calculation is as follows:

With a nomenclature for carbon dioxide similar to that for methane, and with V_w, C_g, and S as constants at 10.00° C., and V'_w, C'_g, and S' as the constants at 10.58° C., then the equilibrium equations are:

At 10.00° C.: $$\frac{V_w}{165}=\frac{(V_t-V_w)S}{31}$$

At 10.58° C.: $$\frac{V'_w}{165}=\frac{(V_t-V'_w)S'}{31}$$

Assume that an air sample free from methane but containing 14 per cent CO_2 is analyzed, and that the temperature drops from 10.58°C. to 10.00°C. during the determination. Then these two equations may be combined and written:

$$CO_2 \text{ absorbed by the water} = V_w - V'_w = \frac{165SV_t}{31+165S} - \frac{165S'V_t}{31+165S'}$$

Substituting the appropriate constants and solving:

$$V_w - V'_w = 0.009 \text{ c. c.}$$

This corresponds to an indication of 0.02 per cent of methane on the scale.

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If the original sample contains carbon dioxide, it will be brought to equilibrium with the water by the preliminary shaking. Therefore the direct contraction due to its solubility will not affect the results; but the dissolved inert carbon dioxide will be replaced by air containing methane if the water level is adjusted to zero, and this will make the reading slightly high. As a probable maximum it may be calculated that carbon dioxide representing 2 per cent of the sample is dissolved in the water of the indicator from the sample during the preliminary shaking. If such a sample is releveled before burning and the sample contains 4 per cent of methane, the indication will be in error by +0.08 per cent of methane, because the 2 per cent of inert gas which was dissolved was replaced by air containing 4 per cent of methane. For smaller methane percentages the error from this cause will be less. Similarly, when an amount of carbon dioxide has been dissolved in the water of the indicator the reading for a sample rich in methane will be low by that same amount because carbon dioxide will come out of solution and prevent a full 31-c. c. sample of the gas from being taken.

Experiments confirmed the conclusion that at constant temperature the amount of carbon dioxide dissolved in the water does not affect the indication appreciably. Gasoline vapor mixed with air was used for these tests because its combustion produces a larger amount of carbon dioxide than does the same amount of methane and any error introduced will be more rapidly cumulative. Accurate analysis with the Haldane apparatus of the special gas mixture used for this experiment showed that it contained 1.27 per cent of gasoline vapor and 0.07 per cent of carbon dioxide, and when burned produced 5.66 per cent of carbon dioxide, calculated on the basis of the original sample.

A series of consecutive analysis of this mixture was made with the indicator, and after every other determination the residual gases were transferred to a Haldane apparatus and the carbon dioxide determined. The carbon dioxide content was interpolated for the intermediate residual gas samples, and the increased amount of carbon dioxide dissolved in the water of the indicator after each determination was calculated by taking the difference between the total amount of carbon dioxide known to be produced by the combustion and that found by analysis of the residual gas. The total volume of carbon dioxide remaining dissolved in the water of the indicator at the end of each determination was calculated and is plotted in Figure 5, with the indications obtained.

When the indicator is in use, the water is saturated with dissolved air, but after it has stood quietly for several hours the dissolved oxygen is removed by electrochemical action on the metals of which the indicator is made; then if pure air is sampled and the indicator

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is shaken, a contraction will be registered on the scale because oxygen from the sample dissolves in the water to replace that previously removed by electrochemical action. This has been proved by testing room air with indicators that originally contained freshly aerated distilled water, but had stood for varying periods. It can be theoretically shown that this contraction may correspond to as much as 1.25 per cent on the methane scale, and during experiments contractions corresponding to 0.92 per cent have been observed.

Fortunately, however, this apparent error is practically eliminated in the operation of the indicator. If shaking the indicator with the gas sample for one minute before combustion brought about equilibrium between the oxygen in the gas and the oxygen dissolved in the water, practically no error would be involved even in the first determination made each day. But in this case equilibrium is not reached so rapidly with all the water in the indicator, and the residual effect that occurs during the final shaking may cause the first indication to be high by perhaps as much as 0.2 per cent of methane. The first reading each day should therefore be discarded. Other readings are not appreciably affected.

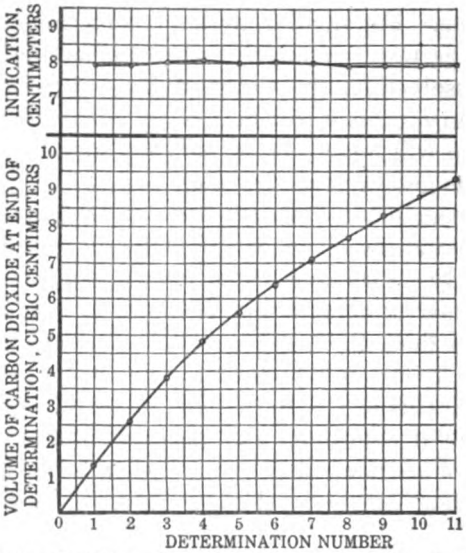

FIGURE 5.—Curves showing that the carbon dioxide content of the water in the indicator does not affect the readings appreciably. Plots of the total dissolved volume of carbon dioxide and the corresponding indications for a series of consecutive determinations made with a sample of air containing gasoline vapor

The air contains oxygen and nitrogen and the partial pressures of these gases change during a combustion because part of the oxygen is removed by combination with the carbon and hydrogen of the methane. However, the changes of partial pressure are proportional to the amount of methane present, and the experimental calibration of the indicator corrects for this factor.

BATTERY VOLTAGE

To heat the glower hot enough to burn the methane completely out of a sample of air in two minutes, the battery voltage must exceed a certain minimum value. Experiments to determine this value, which were made with air samples moderately high in methane, showed that the indication was constant when the drop in potential through the glower circuit between the ends of the indicator cord exceeded 2.3

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volts. (See Fig. 8, p. 26.) A freshly charged Edison M–8 battery, as used with the indicator, has an abnormally high peak voltage which may exceed 3 volts when the battery is removed from the charging apparatus. If used then for the analysis of air samples containing considerable methane, the glower is likely to burn out. After the battery stands two hours or more, much of this excess voltage has gone; therefore only such batteries should be used.

Ten new Edison M–8 batteries were conditioned by charging and discharging them five successive times. They were then fully charged and allowed to stand two hours. Each battery was attached to an indicator and the glowers were burned 2 minutes out of every 15, the voltage at the battery end of the indicator cord being read just after the glower was turned on and again just before it was turned off. Figure 6 gives the average discharge curves thus obtained; and no one battery deviated greatly from the average.

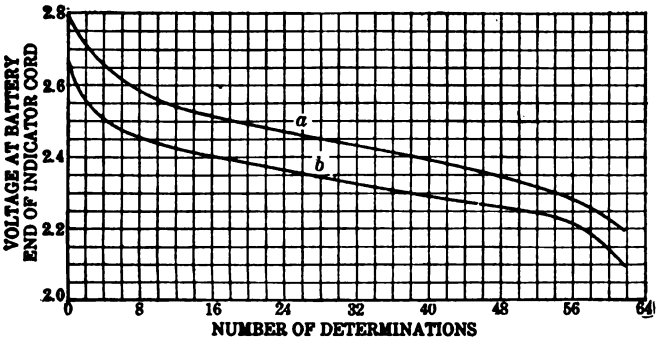

FIGURE 6.—Average discharge curves of 10 Edison M–8 batteries used with Burrell methane indicator for 2 minutes in every 15: *a*, Just after switch was closed; *b*, just before switch was opened

Evidently, under the most favorable conditions 40 determinations can be obtained with an indicator before the battery needs recharging. When the voltage maintained at the end of the indicator cord is less than 2.3 volts during the burning, methane combustion is incomplete.

Some have thought that the indicator could be used in parallel with an electric cap lamp, but this is not satisfactory, because the voltage rapidly falls below 2.3 volts when both devices are attached to one battery and then accurate results are not obtained with the indicator. The development of batteries of larger capacity may make this scheme possible, but official approval has not been extended to cover it as yet.

USE FOR COMBUSTIBLE GASES OTHER THAN METHANE

As stated before and as is well known, the Burrell indicator was originally designed for determining methane in mine air but can be used advantageously for any other single combustible gas or vapor

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present in air in proportions below the explosive limit, if the gas or vapor is practically insoluble in water, is true for as small quantities of hydrogen or the vapor of petroleum hydrocarbons. Hydrogen is generated by the storage batteries of submarines, and frequent analysis of the air in such vessels is essential for detecting accumulations in time to prevent explosions. Around oil refineries, inside empty oil storage-tanks which must be welded, and in sewers there may be dangerous accumulations of the vapor of petroleum hydrocarbons.

When the indicator is used to analyze for one of these gases, their different properties make it necessary to respecify the time of combustion and the minimum battery voltage required. At present, scales for the indicator reading in terms of hydrogen, gasoline vapor, or fuel-oil vapor may be purchased from the manufacturer. In view of the facts discussed later, changes in certain of these scales will probably be advantageous.

HYDROGEN

Hydrogen burns according to the reaction:

$$2\ H_2 + O_2 = 2\ H_2O$$

2 volumes hydrogen + 1 volume oxygen = 0 volume water

Contraction = 1½ times volume of hydrogen

Values of contraction on burning which are calculated from chemical equations apply to the contraction in an accurate gas-analysis apparatus and not to the actual contraction in the indicator, because the latter is modified by factors which have been discussed in detail for methane.

When hydrogen is being determined, the operation of the indicator is similar to that for methane, except that hydrogen is completely burned in one minute and much lower battery voltages, corresponding only to a good red heat for the glower, are satisfactory. These facts are shown graphically in Figures 7 and 8, in which each curve represents a series of analyses of one gaseous mixture.

From Figure 7, in which the period of burning was the only variable, it is seen that hydrogen is completely burned in one minute, that methane requires two minutes, and that gasoline vapor requires four minutes for complete combustion. The hot glower wire produces different temperatures throughout the gas space which set up rapid convection currents; but these alone can not bring all the gas molecules into contact with the wire. The amount of time required in the tests of the three gases apparently depends mainly upon the rate of diffusion of the gases. Since hydrogen is the lightest gas, it diffuses most rapidly to the hot wire, at the surface of which it unites with the oxygen; therefore the combustion of hydrogen requires the least time.

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The set of experiments from which the curves of Figure 8 were plotted were alike, except that the time of burning was kept constant at one minute for hydrogen, two minutes for methane, and four minutes for gasoline vapor, and the voltage applied to the end of the electric cord was varied. These curves show that hydrogen is burned completely at much lower battery voltages (lower glower temperatures) than either gasoline vapor or methane. The minimum satisfactory voltages measured while the glower is burning are

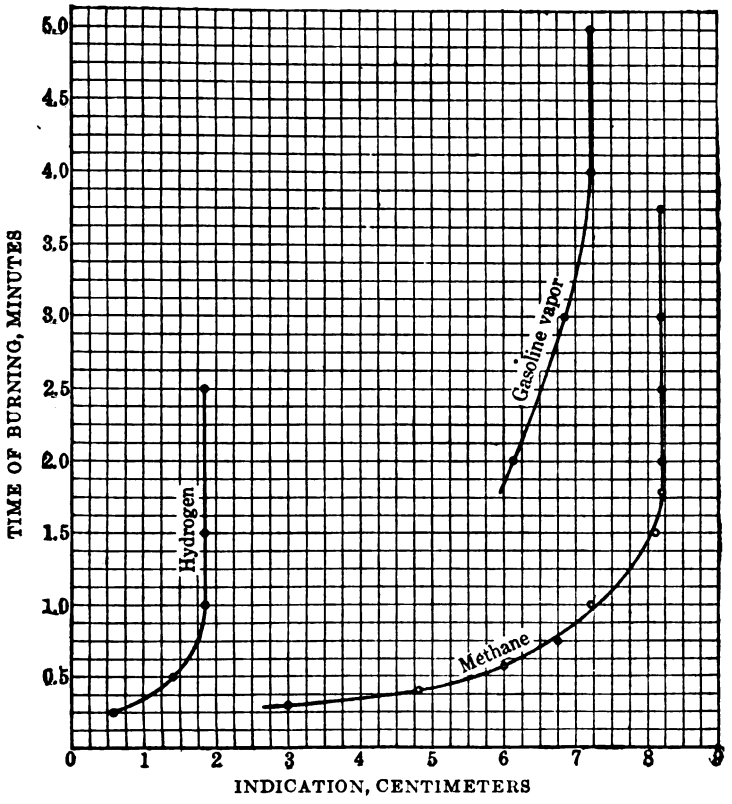

FIGURE 7.—Curves showing the effect of varying time of burning when using the indicator for the analysis of mixtures of different combustible gases with air. The e. m. f. applied to the end of the indicator cord during the burning was 2.3 volts. The straight portions of the curves represent practically complete combustion

approximately 1.5 for hydrogen, 1.8 for gasoline vapor, and 2.2 to 2.3 for methane. Under these circumstances catalysis at the hot platinum surface may be one of the controlling factors.

GASOLINE AND OTHER VAPORS

Gasoline vapor and vapors from such other petroleum hydrocarbons as kerosene and fuel oil differ from the combustible gases previously considered in that each is not a single definite chemical compound but a mixture of compounds that contract somewhat differently

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when burned. Table 5 shows what members of the paraffin series may be present in the vapors from petroleum hydrocarbons. The values of the contraction on burning refer to the contraction which takes place in an accurate apparatus for gas analysis, and not to the actual contraction which takes place in the Burrell indicator.

TABLE 5.—*Data on the complete combustion of the paraffin hydrocarbons*

Hydrocarbon	Formula	Boiling point of liquid °C.	Per 1 volume of hydrocarbon		
			Volume of O_2 required	Volume of CO_2 produced	Volume of contraction
Ethane	C_2H_6	−84	3.5	2	2.5
Propane	C_3H_8	−45	5.0	3	3.0
Butane	C_4H_{10}	0	6.5	4	3.5
Pentane	C_5H_{12}	+37	8.0	5	4.0
Hexane	C_6H_{14}	69	9.5	6	4.5
Heptane	C_7H_{16}	98	11.0	7	5.0
Octane	C_8H_{18}	126	12.5	8	5.5

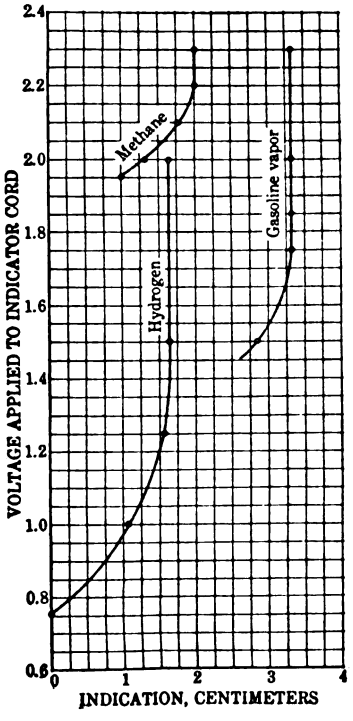

FIGURE 8.—Curves showing the effect of varying the voltage applied to the end of the indicator cord when using the indicator for the analysis of mixtures of different combustible gases with air. Time of burning—H_2=1 minute; CH_4=2 minutes; gasoline vapor=4 minutes. The straight portions of the curves represent practically complete combustion

Gasoline vapor is typically a mixture of paraffin hydrocarbons between butane and heptane, but analyses by the gas laboratory of the Bureau of Mines have shown that the average composition of the vapors given off in tanks which have contained gasoline, crude oils, and so on, may vary from ethane to octane. Hydrocarbons higher than octane have such low vapor pressures that they can not exist in appreciable amounts as vapor in the air at ordinary temperatures.

A scale for the indicator calibrated for one sample of gasoline or fuel-oil vapor therefore will hardly be correct for the percentage analysis of vapors from other samples. The gasoline vapor scale now supplied for the indicator was made by actual calibration with the vapor from a gasoline sample which was considered to be typical, and it was assumed that the analysis of air containing any gasoline vapor would then be interpreted in terms of this typical sample. However, in any given circumstances the true percentage of gasoline vapor present in the air and that indicated on this scale is liable to show wide difference.

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In connection with the investigation of the vapors given off by fuel oil, G. W. Jones, gas chemist at the Pittsburgh experiment station, has suggested the use of a scale showing the "relative explosibility" of petroleum vapors, this term being applied to vapor and gases from gasoline and other petroleum products as well as petroleum. When the indicator is used for petroleum vapors the operator wants to know how safe the conditions are; he does not care what absolute quantity of a given hydrocarbon vapor is in the air as long as it is small enough to remove the possibility of dangerous explosive conditions. It is particularly fortunate that the mixtures of different petroleum vapors with air will all give very nearly the same reading on the indicator when the mixture corresponds to the lower explosive limit of the particular hydrocarbon present. Therefore an arbitrarily graduated scale can be approximately interpreted in terms of relative explosibility for all of the paraffin hydrocarbons from ethane to octane independent of the absolute percentage present, as is shown by the calculation in Table 6. This is discussed in more detail in the next section.

TABLE 6.—*Approximate calculation of the relative indications obtained with the Burrell indicator when used to analyze mixtures of paraffin hydrocarbons and air at the lower explosive limit*

(a) Hydrocarbon gas formula	(b) Theoretical contraction per c. c. of gas	(c) CO_2 produced per c. c. of gas	(d) Contraction due to CO_2 solubility in indicator per c. c. of gas [0.83×(c)][a]	(e)=(b)+(d) This is approximately proportional to contraction in indicator per c. c. of gas	(f) Gas present at lower explosive limit [b]	(g)=(e)×(f) A figure approximately proportional to contraction in indicator with an explosive mixture [d]
	C. c.	*C. c.*	*C. c.*	*C. c.*	*Per cent*	
C_2H_6	2.5	2	1.66	4.16	3.10	12.9
C_3H_8	3.0	3	2.49	5.49	2.17	11.9
C_4H_{10}	3.5	4	3.32	6.82	1.65	11.3
C_5H_{12}	4.0	5	4.15	8.15	1.35	11.0
C_6H_{14}	4.5	6	4.98	9.48	[c](1.15)	10.9
C_7H_{16}	5.0	7	5.81	10.81	[c](0.99)	10.7
C_8H_{18}	5.5	8	6.64	12.14	[c](0.87)	10.6

[a] The factor 0.83 is approximately the ratio at 25° C., after shaking the indicator vigorously for one minute, between the CO_2 dissolved and the total CO_2 produced by the combustion

$$\frac{0.875}{1.055}=0.83$$ (See p. 30).

[b] See Burgess, M. J., and Wheeler, R. V., The lower limit of inflammation of mixtures of the paraffin hydrocarbons with air: Jour. Chem. Soc., vol. 99, 1911, pp. 2013–2030.

[c] Parentheses inclose calculated values.

[d] This table is based on the specific assumption that no other variables come in—that is, that these gases all dissolve in water to the same relative extent, etc.—and since this is not exactly true, the figures in column (g) are only approximate.

CALIBRATION OF THE INDICATOR

The indicator for the combustible gases—methane, hydrogen, and gasoline vapor—was first calibrated experimentally. This procedure was best at that time, but the weakness of such calibration for any instrument without consideration of the theory involved is due to

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the assumption that the conditions of use will exactly duplicate those prevailing during the calibration—something that may never be exactly true. Experimental calibration tells nothing of the source or probable magnitude of errors, and hence may be unreliable.

The following discussion, therefore, treats both the theoretical and the experimental calibration of the indicator. An attempt is made to point out possible errors and to evaluate their probable maximum magnitude; to show how they may be avoided, what the true form of the scales for the indicator should be, and (by means of an illustration with methane), how a calibration for the indicator may be calculated for a combustible gas not considered here. This discussion shows why extremely accurate results can not be expected. The calculations are carried through in detail for methane, and are summarized for hydrogen and gasoline vapor.

THEORETICAL CALIBRATION FOR METHANE

In the development of a theoretical calibration for the Burrell methane indicator the following factors must be considered:

1. The methane dissolved or liberated by the water of the indicator.
2. The carbon dioxide dissolved or liberated by the water of the indicator.
3. The nitrogen dissolved by the water of the indicator.
4. The oxygen dissolved or liberated by the water of the indicator.
5. The reduced pressure under which the residual gases are measured, the difference in pressure being equivalent to the difference in level between the water surface in the gage glass and in the large tube when the final reading is taken.
6. The heat liberated by the glower.

Two general assumptions are made: First, that the indicator is correctly proportioned and properly used; and second, that at the beginning of a determination on air containing methane, the indicator is at air temperature, and the only temperature change during a determination is due to the constant amount of heat which the glower adds. It has already been shown before that shaking the indicator for one minute brings about gaseous equilibrium with the water in the large reservoir plus 50 per cent of the water in the small reservoir and gage glass, and that the methane is practically completely burned to carbon dioxide and water.

The first five factors given above are proportional to the amount of methane in the sample, and the sixth is constant; therefore the calibration curve is a straight line. Calculation is made only for the maximum methane-air mixture which may be analyzed—a 4 per cent methane sample—and a straight line is drawn which represents the indications obtained with intermediate mixtures. The effect due to the first three factors is primarily assumed to take place at atmospheric pressure, and the result is then corrected to the reduced pressure which actually prevails when the reading is made; finally, allowance is made for the constant

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heat effect of the glower. The calculation is made for two temperatures—10° and 25° C.—which approximate the two conditions of operation which the indicator has to meet. Comparison of these two calculations shows directly just what accuracy may be expected if the indicator is used first at one temperature and then at the other, or if it is calibrated at one temperature and used at the other. The detailed calculation for methane follows:

At first the water in the indicator is saturated with air of normal composition as follows:

	At 10° C. *Per cent*	At 25° C. *Per cent*
Water vapor	1. 21	3. 10
Oxygen	20. 65	20. 25
Nitrogen	78. 14	76. 65

The volumes of the dissolved oxygen and nitrogen in 165 c. c. of water in equilibrium with this air may therefore be calculated from the formula: $\frac{V_w}{165} = C_g \times S$, and are found to be,

	At 10° C. *C. c.*	At 25° C. *C. c.*
V_w for oxygen	1. 342	1. 033
V_w for nitrogen	2. 620	2. 075

A sample of saturated air containing 4 per cent of methane has the composition,

	At 10° C. *C. c.*	*Per cent*	At 25° C. *C. c.*	*Per cent*
Methane	1. 240	= 4. 00	1. 240	= 4. 00
Water vapor	0. 375	= 1. 21	0. 962	= 3. 10
Oxygen	6. 14	= 19. 80	6. 02	= 19. 42
Nitrogen	23. 24	= 74. 99	22. 78	= 73. 48

Assume that the entire 31 c. c. of this air sample containing 4 per cent of methane is taken into the indicator and shaken for one minute. As was shown in the discussion of the solubility of methane in the water of the indicator, part of the methane goes into solution; that is,

	At 10° C. *C. c.*	At 25° C. *C. c.*
V_w for methane	0. 233	0. 185
V_g for methane	1. 007	1. 055

The total volume of oxygen and nitrogen present (dissolved in 165 c. c. of water plus gas) is:

	At 10° C. *C. c.*	At 25° C. *C. c.*
Total volume of oxygen	7. 48	7. 05
Total volume of nitrogen	25. 86	24. 86

and this redistributes itself after shaking according to the formula,

$$\frac{V_w}{165} \div \frac{V_t - V_w}{31.00} = S$$

	At 10° C. *C. c.*	At 25° C. *C. c.*
V_w for oxygen	1. 297	0. 996
V_g for oxygen	6. 18	6. 05
V_w for nitrogen	2. 520	1. 995
V_g for nitrogen	23. 34	22. 86

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If the water level in the gage glass is brought to zero on the scale, and the composition of the gas sample becomes

	At 10° C.		At 25° C.	
	C. c.	*Per cent*	*C. c.*	*Per cent*
Methane	1. 007	= 3. 25	1. 055	= 3. 40
Water vapor	0. 375	= 1. 21	0. 962	= 3. 10
Oxygen	6. 20	=20. 00	6. 05	=19. 50
Nitrogen	23. 42	=75. 54	22. 93	=74. 00

The combustion burns the methane completely, removing a volume of oxygen equal to twice that of the methane and producing a volume of carbon dioxide equal to that of the methane. The final shaking dissolves some carbon dioxide and nitrogen, and causes some oxygen and methane to come out of solution.

The contraction due to the combustion itself is 2.014 c. c. at 10° C. and 2.110 c. c. at 25° C. Approximate preliminary calculation shows that about 0.88 c. c. of carbon dioxide is dissolved by the water, 0.17 c. c. of methane comes out of solution, 0.26 c. c. of oxygen comes out of solution, and 0.20 c. c. of nitrogen goes into solution. The approximate net contraction is therefore 2.70 c. c.; which corresponds to a residual gas volume of 28.3 c. c., this volume will therefore be used as a basis for calculating the exact magnitude of these quantities which are calculated from the equilibrium formula:

$$\frac{V_w}{165}+\frac{V_t-V_w}{28.3}=S.$$

The total volumes of the gases present (dissolved plus gas) are:

V_t for—	At 10° C. C. c.	At 25° C. C. c.
Methane	0. 233	0. 185
Carbon dioxide	1. 007	1. 055
Oxygen	5. 49	4. 94
Nitrogen	25. 94	24. 93

The volumes of these gases dissolved in the water at the equilibrium resulting from shaking after combustion are:

V_w for—	At 10° C. C. c.	At 25° C. C. c.
Methane	0. 047	0. 030
Carbon dioxide	0. 885	0. 875
Oxygen	1. 026	0. 755
Nitrogen	2. 745	2. 174

The volumes of these gases which were present in the water just before combustion were:

	At 10° C. C. c.	At 25° C. C. c.
Methane in water before combustion	0. 233	0. 185
Carbon dioxide in water before combustion	0. 000	0. 000
Oxygen in water before combustion	1. 297	0. 996
Nitrogen in water before combustion	2. 520	1. 995
Contraction due to CO_2	0. 885	0. 875
Contraction due to N_2	0. 225	0. 179
Sum	1. 110	1. 054
Expansion due to methane	0. 186	0. 155
Expansion due to oxygen	0. 271	0. 241
Sum	0. 457	0. 396
Net contraction—difference	0. 653	0. 658
Previous contraction	2. 014	2. 110
Corrected total contraction at atmospheric pressure	2. 667	2. 768

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In order to calculate what the contraction will actually be under the reduced pressure which prevails in the indicator the following formula has been developed:

Let x be the number of cubic centimeters between zero and the final reading of the indicator. Then with the large gage glass of cross-sectional area 0.246 sq. cm., the actual contraction under reduced pressure is $0.246x$ c. c. The cross-sectional area of the collar in the large reservoir where the water level stands is 3.80 sq. cm.; therefore the water level will rise $\frac{0.246x}{3.8}=0.0648x$ centimeter at this point. Let the residual gases occupy a volume, z', under 76 cm. of mercury, and let them actually occupy a volume z under the pressure of

$$76-\frac{(x+0.0648x)}{(13.6)}=76-0.0783x \text{ cm. of mercury.}$$

The actual contraction under reduced pressure is,

$$31-z=0.246x$$

or,

$$z=31-0.246x.$$

The contraction under 76 cm. of mercury is $31-z'$.

But, $\frac{z}{z'}=\frac{76}{76-0.0783x}$, and therefore substituting and solving:

$$z'=31-0.278x+0.000253x^2$$

$$\text{The contraction at 76 cm. pressure}=31-z'=0.278x-0.000253x^2 \quad (1)$$

$$\text{But the actual contraction under reduced pressure}=0.246x \quad (2)$$

Dividing (2) by (1), and simplifying:

$$\text{Actual contraction under reduced pressure}=\frac{\text{Contraction at 76 cm. pressure}}{1.130-0.001028x} \quad (3)$$

In order to remove x from expression (3), its value may be approximated from (1) by neglecting the x^2 term which has a value of less than 1 per cent of the x term, when the values of x are less than 10; in which case

$$x=\frac{\text{Contraction at 76 cm. pressure}}{0.278}.$$

Substituting in (3) gives,

$$\text{Actual contraction under reduced pressure} =$$

$$\frac{\text{Contraction at 76 cm. pressure}}{1.130-(0.0037)(\text{Contraction at 76 cm. pressure})}$$

Applying this formula, it is found that the actual contraction under reduced pressure at 10° C. is 2.380 c. c. and at 25° C. 2.470 c. c.

These values are divided by the sectional area of the gage glass to get the indication not corrected for the heat from the glower, which is 9.67 cm. at 10° C. and 10.03 cm. at 25° C.

The constant heat effect of the glower was determined experimentally by analyzing samples of room air, and an average expansion of 0.25 cm. was registered on the scale for a two-minute burn. Corrected for this, the indications become 9.42 cm. at 10° C. and 9.78 cm. at 25° C.

The values derived by this calculation represent the first indication obtained when distilled water saturated with air is used in the indi-

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cator. Since it is desired to have the calibration most accurate for the second determination on the same gas mixture, the values must be slightly modified, for even after the shaking that follows the first determination a small amount of methane will be left dissolved in the water; and when the next sample is taken this methane will be distributed throughout all of the 190 c. c. of water in the indicator, and 165 c. c. of this water will be brought to equilibrium with the new gas sample. The fact that this water already contains a small amount of methane will cause a slightly smaller volume of methane than has been calculated to go into solution during the first shaking with the new sample. This effect is proportional to the amount of methane present in the air sample, and its effect on the indication can be calculated from previous results.

	At 10° C.	At 25° C.
(*a*) Methane dissolved per 190 cubic centimeters----c. c--	0. 047	0. 030
(*b*) Methane dissolved per 165 cubic centimeters----c. c--	0. 041	0. 026
(*c*) Methane extracted on shaking----c. c--	0. 033	0. 022
(*d*) Increase in indication----cm--	0. 31	0. 21
(*e*) Final theoretical indication----cm--	9. 73	9. 99

This final theoretical indication is the approximate value which should be obtained by the second and subsequent consecutive determinations with a 4 per cent methane sample. The theoretical calibration of the indicator is shown as a curve in Figure 9.

A theoretical calibration was calculated for the methane indicator when fitted with the small gage glass. This was easily done because the small gage glass has a cross sectional area just half that of the large one; therefore the corrected total contraction at atmospheric pressure for a 2 per cent methane sample is just half of the value calculated for the 4 per cent sample. The formula for calculating the actual contraction under reduced pressure was derived similarly to that for the large gage glass, using the area 0.123 sq. cm.:

$$\text{Actual contraction under reduced pressure} = \frac{\text{Contraction at 76 cm. pressure}}{1.252-(0.0065)(\text{contraction at 76 cm. pressure})}$$

When this is applied, results are:

Data on contraction

	At 10° C.	At 25° C.
(*a*) Corrected total contraction at atmospheric pressure--c. c--	1. 334	1. 384
(*b*) Actual contraction under reduced pressure----c. c--	1. 072	1. 113
(*c*) Indication not corrected for heat from glower= (*b*) +0.123----cm--	8. 71	9. 05
(*d*) Indication corrected for glower effect=(*c*)−0.50----cm--	8. 21	8. 55
(*e*) Increase in second indication due to dissolved methane----cm--	0. 29	0. 19
(*f*) Final theoretical indication----cm--	8. 50	8. 74

A line representing the theoretical methane calibration for the small gage glass is shown in Figure 9.

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EXPERIMENTAL CALIBRATION FOR METHANE

Mixtures of Pittsburgh natural gas and air were analyzed with a carefully constructed indicator (No. 340), which took the correct 31-c. c. sample and could be fitted interchangeably either with a large gage glass of 5.59 mm. average diameter or a small one of 3.94 mm. average diameter. Current for heating the glower was obtained from a five-cell storage battery connected through an adjustable resistance, and a voltmeter indicated the potential difference at the end of the electric cord of the indicator. A potential difference of 2.35 volts was maintained during the burning.

The gas mixtures were confined in a bottle over water. Accurate determinations of the equivalent methane in the samples were made with the Haldane gas-analysis apparatus as described before; closely agreeing duplicate analyses were obtained for each mixture. As would be expected for the rich mixtures, the first reading when the indicator contained fresh water was slightly lower than subsequent readings. Since calibration should be accurate for the second and subsequent readings, the first reading was discarded and is not tabulated. The actual results are given in Tables 7 and 8, and the averages are plotted as points in Figure 9, with curves representing the theoretical calibration of the indicator and curves representing the present scales which the manufacturer supplies for the indicator.

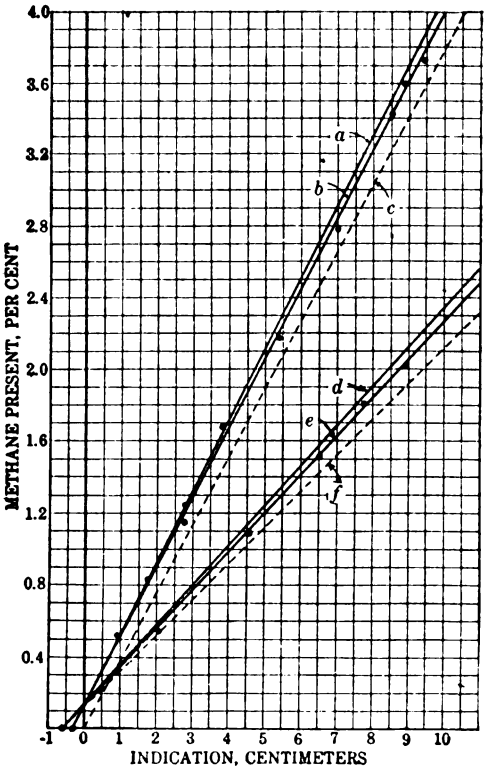

FIGURE 9.—Calibration of the indicator for methane (shaking one minute both before and after combustion and burning for two minutes at 2.35 volts): *a*, Theoretical calibration for the large gage glass at 10° C.; *b*, theoretical calibration for the large gage glass at 25° C.; *c*, present calibration for the large gage glass; *d*, theoretical calibration for the small gage glass at 10° C.; *e*, theoretical calibration for the small gage glass at 25° C.; *f*, present calibration for the small gage glass. The points represent the average of actual analyses made with the indicator, at 25° C., as given in Tables 7, 8, and 9

These results verify the soundness of the general theory. They show that the present methane scales are slightly in error due, first, to overlooking the heating effect of the glower in the design of the present scale for the large gage glass; second, to the fact that when the

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old calibration was made, the indicator was only shaken with the sample for one-half minute before combustion, a length of time which was thought then to be ample but has since been determined to be too short; and third, to the fact that Pittsburgh natural gas was used for the old calibration, and the results of Haldane analysis were calculated to "total hydro carbons," which was called "per cent methane." The more correct method of calculating "equivalent methane," which was used in the present tests, has been given on page 11. The tendency of experimental results for pure methane in mines to be slightly low (see Tables 1 and 2) bears out this conclusion.

TABLE 7.—*Experimental calibration at 25° C. of the methane indicator fitted with large gage glass*

Sample No.	Indicator reading				Equivalent CH_4 present
	Before burning	After burning	Corrected	Average	
	Mm.	*Mm.*	*Mm.*	*Mm.*	*Per cent*
1a	−0.5	71.5	72.0	70.0	2.75
b	0.0	68.5	68.5		
c	−4.0	65.5	69.5		
2a	−2.5	35.0	37.5	37.8	1.66
b	0.0	38.0	38.0		
c	−1.3	36.7	38.0		
3a	0.0	29.0	29.0	28.0	1.25
b	+1.3	29.3	28.0		
c	0.0	27.0	27.0		
4a	+1.0	18.5	17.5	17.8	0.84
b	−3.0	15.5	18.5		
c	+4.0	21.5	17.5		
5a	+2.5	11.5	9.0	9.5	0.54
b	−2.0	8.0	10.0		
c	+4.0	13.5	9.5		
6a	−4.0	83.0	87.0	86.1	3.42
b	−2.5	84.5	87.0		
c	−1.3	83.2	84.5		
7a	+4.5	59.0	54.5	54.0	2.17
b	−1.3	52.7	54.0		
c	−2.0	51.5	53.5		
8a	0.0	−4.0	−4.0	−2.0	0.00
b	+1.3	−1.3	−2.6		
c	−2.5	−5.0	−2.5		
9a	+1.3	88.3	87.0	89.0	3.60
b	+4.5	94.5	90.0		
c	+5.0	95.0	90.0		

TABLE 8.—*Experimental calibration at 25° C. of the methane indicator fitted with small gage glass*

Sample No.	Indicator reading				Equivalent CH_4 present
	Before burning	After burning	Corrected	Average	
	Mm.	*Mm.*	*Mm.*	*Mm.*	*Per cent*
1a	0.0	−5.0	−5.0	−5.5	0.00
b	+0.5	−6.5	−7.0		
c	−0.5	−5.0	−4.5		
2a	−0.5	88.0	88.5	89.0	2.02
b	−2.5	88.0	90.5		
c	+5.5	90.0	84.5		
d	−4.0	88.5	92.5		
3a	+5.0	80.0	75.0	78.0	1.81
b	+5.0	83.5	78.5		
c	−2.5	77.5	80.0		
d	+1.3	79.8	78.5		
4a	−2.0	64.0	66.0	65.2	1.51
b	+7.0	72.0	65.0		
c	−2.5	62.0	64.5		
5a	−2.0	44.0	46.0	45.5	1.09
b	−4.5	41.0	45.5		
c	0.0	45.0	45.0		
6a	−2.5	18.5	21.0	20.8	0.53
b	0.0	20.5	20.5		
c	+8.0	29.0	21.0		

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In order to confirm this fact further, and to obtain data on the use of an indicator by different operators, mixtures of pure methane and air were made up and analyzed. The methane was prepared from dry Pittsburgh natural gas by passing it through absorbent coconut charcoal cooled in an ice bath. Accurate analysis showed the unabsorbed gas to be pure methane. The results obtained with indicator No. 127 fitted with a gage glass of 5.59 mm. inside diameter, and attached to a fully charged Edison portable M–8 battery, appear in Table 9.

TABLE 9.—*Analysis of mixtures of pure methane and air, with the indicator fitted with large gage glass, at 25° C*

Sample No.	Reading			Observer	Average reading	Methane present
	Before burning	After burning	Corrected			
	Mm	*Mm.*	*Mm.*		*Mm.*	*Per cent.*
1a	0.0	93.0	93.0	A		
b	−4.0	88.0	92.0	A		
c	−3.0	91.5	94.5	A		
d	−2.0	88.5	90.5	B		
e	−6.5	83.5	90.0	B	94.0	3.73
f	−3.5	93.0	96.5	A		
g	−3.5	92.5	95.5	A		
h	−6.5	90.5	97.0	C		
i	−3.5	95.0	98.5	D		
j	+1.5	94.5	93.0	D		
2a	+1.0	29.0	28.0	A		
b	−0.5	27.5	28.0	A		
c	+2.0	28.5	26.5	A	27.5	1.15
d	+1.0	29.5	28.5	B		
e	0.0	26.5	26.5	B		

NOTE.—Fresh water was placed in the indicator before sample 1a and between samples 1i and 1j, and between 2b and 2c. The first readings obtained after fresh water was put in are not tabulated, but were 91 and 89 mm. for sample 1 and 25 mm. for sample 2.

The points representing the averages of these results have been plotted in Figure 9, and lie approximately on the theoretical curve. The readings obtained by different observers do not diverge widely. The differences are chiefly due to variations in the intensity of the shaking which precedes and follows the combustion, and are at a minimum when the shaking is vigorous.

The difference between the results which will be obtained with the indicator at 10° and 25° C. is small and does not limit the usefulness of the instrument.

THEORETICAL AND EXPERIMENTAL CALIBRATION FOR HYDROGEN

A theoretical calibration for the indicator, calculated for hydrogen, leads to the following values:

Theoretical scale reading

	At 10° C. *Mm.*	At 25° C. *Mm.*
Large gage glass for 6 per cent H_2	8.93	8.90
Small gage glass for 3 per cent H_2	7.92	7.88

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Results obtained with the indicator as ordinarily used for mixtures of hydrogen in air are therefore practically independent of the particular temperature at which the determinations are made, so long as the temperature remains constant. Curves for these theoretical calibrations have been drawn in Figure 10. Actual results obtained in the laboratory with the indicator are given in Tables 10 and 11, and the averages have been plotted as points in Figure 10. The dotted lines *b* and *d* in the figure represent the scale for hydrogen with which the indicator is now supplied.

TABLE 10.—*Experimental calibration at 25° C. of the hydrogen indicator fitted with large gage glass*

Sample No.	Reading				Hydrogen present
	Before burning	After burning	Corrected	Average	
	Mm.	*Mm.*	*Mm.*	*Mm.*	*Per cent*
1a	+2.0	87.0	85.0	85.5	5.81
b	+1.3	87.0	85.7		
c	+5.0	90.7	85.7		
2a	+2.0	83.8	81.8	81.7	5.71
b	−1.3	79.7	81.0		
c	0.0	82.2	82.2		
3a	+2.5	85.5	83.0	83.1	5.71
b	+3.0	86.3	83.3		
c	−0.5	83.5	84.0		
d	+2.0	83.9	81.9		
4a	+2.0	85.0	83.0	83.5	5.64
b	+3.3	88.1	84.8		
c	+3.0	87.3	84.3		
d	+4.0	85.8	81.8		
5a	+5.0	54.5	49.5	49.2	3.43
b	+1.3	50.0	48.7		
c	+2.2	51.7	49.5		
6a	+3.5	35.0	31.5	31.5	2.30
b	+3.7	35.2	31.5		
7a	+3.0	20.2	17.2	16.7	1.24
b	−1.5	14.5	16.0		
c	−2.5	14.5	17.0		

These results confirm the theory and show that the hydrogen scale at present supplied with the indicator is substantially correct when the gage glass is of the correct diameter, the volume of the sample is 31 c. c., and the one-minute period of combustion is both preceded and followed by a one-minute period of thorough shaking.

TABLE 11.—*Experimental calibration at 25° C. of the hydrogen indicator fitted with small gage glass*

Sample No.	Reading				Hydrogen present
	Before burning	After burning	Corrected	Average	
	Mm.	*Mm.*	*Mm.*	*Mm.*	*Per cent*
1a	0.0	92.0	92.0	92.0	3.43
b	+0.5	92.3	91.8		
c	+2.0	94.2	92.2		
2a	+1.3	61.9	60.6	59.5	2.30
b	+6.5	65.3	58.8		
c	+4.0	63.0	59.0		
3a	+2.0	34.0	32.0	31.1	1.24
b	+1.3	31.5	30.2		
4a	0.0	−2.5	−2.5	−2.5	0.00
b	0.0	−2.5	−2.5		

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THEORETICAL AND EXPERIMENTAL CALIBRATION FOR GASOLINE VAPOR

To ascertain more accurately the reading which should be obtained when the indicator is used in analyzing petroleum vapors and to get theoretical calibrations for hexane (C_6H_{14}) and for heptane (C_7H_{16}) at 25° C., calculations were made similar to those for methane. No data for the solubility of these gases in water at 25° C. could be found in the literature; therefore the solubilities of the vapors from two different samples of gasoline were determined for use in making the calculation and have been given in Table 4 (p. 17). The calculation of the theoretical calibration for hexane and heptane leads to the following values:

	1 per cent hexane	1 per cent heptane
Theoretical scale reading at 25° C.....cm..	8.82	9.65

This is calculated for a four-minute burn, which is assumed to give complete combustion.

Figure 11 presents curves representing the theoretical calibration for heptane, hexane, and methane. No solubility data were obtained for other hydrocarbons, and it was therefore impossible to calculate for them accurately; but the lines for the hydrocarbons between hexane and methane were so drawn as to make equal divisions of the interval, and the line for octane was drawn as far beyond heptane as that for heptane is beyond hexane. This procedure of interpolation and extrapolation should be accurate enough for the purpose.

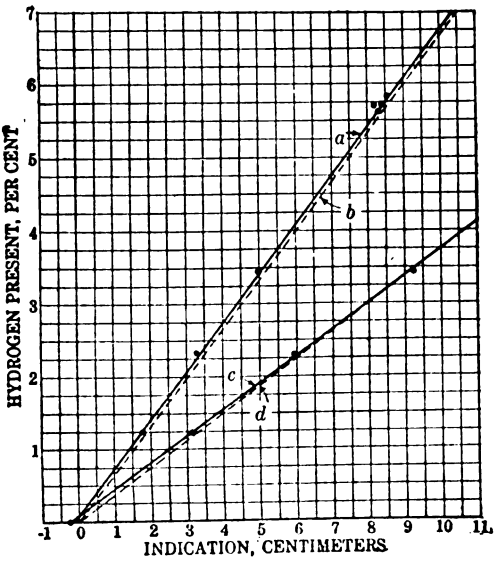

FIGURE 10.—Calibration of the indicator for hydrogen (shaking one minute both before and after combustion, and burning for one minute at 2.3 volts): *a*, Theoretical calibration for the large gage glass 10° to 25° C.; *b*, present calibration for the large gage glass; *c*, theoretical calibration for the small gage glass, 10° to 25° C.; *d*, present calibration for the small gage glass. The points represent the average of actual analyses with the indicator at 25° C., as given in Tables 10 and 11

Analyses with the indicator of four air samples containing gasoline vapor gave the results presented in Table 12, the averages of which have been plotted as points in Figure 11. The time of burning was four minutes, and the indicator was shaken for one minute before and after combustion. The points fall within the region of the figure that corresponds to their composition.

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TABLE 12.—*Analysis of samples of air containing gasoline vapor at 25° C., indicator fitted with large gage glass*

Sample No.	Kind of gasoline	Reading				Total hydrocarbons present
		Before burning	After burning	Corrected	Average	
		Mm.	*Mm.*	*Mm.*	*Mm.*	*Per cent*
A1	Casing head	−1.5	78.0	79.5		
2	do	0.0	79.5	79.5	77.4	0.89
3	do	0.0	74.0	74.0		
4	do	0.0	76.5	76.5		
B1	do	0.0	54.5	54.5		
2	do	−3.0	51.0	54.0	54.1	0.70
3	do	−0.5	53.5	54.0		
C1	Motor	−0.5	71.0	71.5		
2	do	+2.0	71.5	69.5	70.7	0.72
3	do	−5.0	66.0	71.0		
D1	do	+4.0	49.0	45.0	45.0	0.47
2	do	0.0	45.0	45.0		

On the curves in Figure 11 the lower explosive limits of the hydrocarbons have been marked with a cross, and are connected with a smooth dotted line which is almost straight and, with the exception of its lower end, is nearly vertical. From this evidence a scale of relative explosibility for petroleum vapors of average composition ranging between propane and octane would be approximately accurate if the "explosive" point was selected about 9.5 cm. from the zero on the indicator scale. The only gas that might seem from the data at hand to give an explosive mixture for a reading slightly less than this is octane, which has such a low vapor pressure that higher temperatures than ordinarily exist would be required to get such a mixture. For the hydrocarbons below heptane the true explosive point would be slightly beyond that shown on the scale, and the true conditions would be slightly safer than the indicator shows.

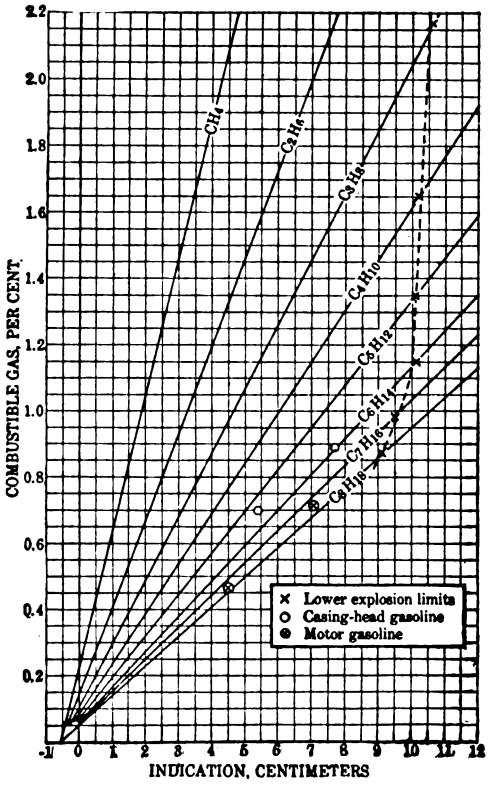

FIGURE 11.—Theoretical calibration curves for the Burrell indicator, fitted with large gage glass, for hydrocarbons between methane and octane at 25° C.

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SUMMARY AND CONCLUSIONS

This paper has discussed in detail the Burrell methane indicator for combustible gases, and especially its use for the determination of methane in mine air; has described the instrument and given instructions for its operation for methane; and has presented typical results of mine tests with it. A modification of the switch design of the indicator, which aims to increase the life of the glower, has been described. The possible sources of error in determinations made with the indicator have been considered, so that there can be no misunderstanding concerning the possibilities and limitations of the instrument. The use of the indicator for hydrogen and for gasoline and other petroleum hydrocarbon vapors has been considered, and the slight differences between the operation of the instrument for those gases and for methane have been discussed. Data for accurate experimental calibration of the indicator have been tabulated, and it has been shown that the calibration can be deduced theoretically from a quantitative consideration of the various factors involved.

The Burrell indicator for combustible gases is so operated that further increase in the accuracy of the present instrument by changing its design or method of operation seems impossible. As it stands, however, it is a useful instrument in its own field, and experienced operators can often obtain surprisingly accurate results. Its satisfactory use for the determination of any one combustible gas in air, requires that this gas be practically insoluble in water. Benzene vapor is quite soluble in water; therefore the indicator can not be used for it. The determination of hydrogen is the simplest and most accurate; first, because this gas is completely and rapidly burned at very low glower temperatures, and secondly, because the combustion produces no carbon dioxide, which is a complicating factor on account of its solubility. The combustion of methane requires a moderate length of time, a high glower temperature is necessary, and some carbon dioxide is produced. Petroleum vapors burn completely with moderate glower temperatures, but require a longer time for complete combustion and produce larger quantities of carbon dioxide.

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